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A SELECT COURSE
IN
QUALITATIVE ANALYSIS,

BY

HENRY A. WEBER, Ph.D.

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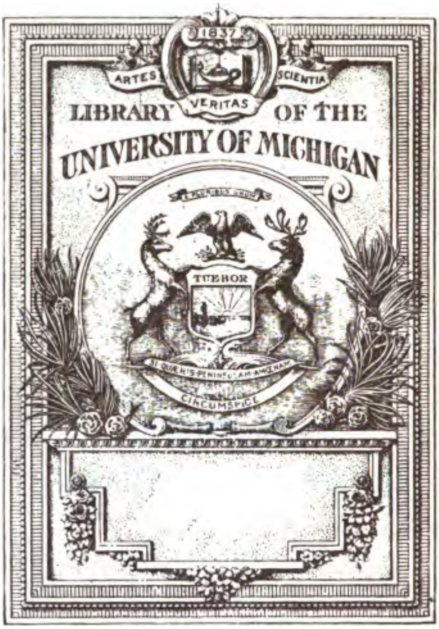

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SELECT COURSE

IN

QUALITATIVE ANALYSIS.

BY

HENRY A. dam WEBER, PH. D., 1845-

PROFESSOR OF CHEMISTRY AT THE ILLINOIS INDUSTRIAL UNIVERSITY.

CHAMPAIGN, ILL.:
PETERSON & LLOYDE,
1880.

PREFACE.

It has been the custom for a number of years past in my own classes, that not only the special students in chemistry, but also those, who pursue the study of chemistry as a part of other courses, take a course in qualitative analysis in connection with the usual class work in elementary chemistry. To meet the wants of the latter class of students especially, the work embraced in the following pages has been laid down. Special students in chemistry will naturally supply themselves with the elaborate and standard works of Fresenius, Douglas and Prescott, &c., and will necessarily become acquainted in their advanced work with the reactions and chemical substances here omitted.

H. A. W.

384307

GENERAL INSTRUCTIONS.

The student begins with the bases of Group I, and makes the tests as laid down for each metal. After each test is made, the reaction, which takes place, is carefully expressed in writing, using the symbols or formulæ of the substances employed. When the tests for the whole group have thus been made, a number of unknown substances, containing only the metals of the group are furnished the student, and he proceeds to determine the respective base of each substance by following the instructions given in the "Table for Testing," and reports the results to the instructor.

Next he receives a solution containing all the bases of the group, and separates them according to the directions given for the " Separation of the Group."

The other groups are then taken up in their proper order and treated in a similar manner. Those substances which are not contained in the list of desk chemicals are supplied from the store room.

The tests for the acids are next made, the reactions being written out as in the case of the bases, after which the analysis of substances is taken up.

The first twenty substances are simple salts, and are selected so as to give as wide a range as possible both in [illegible] to bases and acids. Then follow twenty complex substances, among which are a number of alloys.

Each desk should be furnished with the following list of apparatus and reagents.

1 Iron stand.
1 Filter stand.
1 Bunsen burner.
5 Feet rubber tubing.
2 Sand baths.
1 Water bath.
1 Pair pincers.
1 Pair tongs.
1 Blow pipe.
1 Nest of seven or eight beakers.
12 Test tubes.
1 Test tube rack.
3 Watch glasses.
1 Platinum foil.
1 Platinum wire.
1 Wash bottle.
2 Funnels.
2 Stirring rods.
1 Mortar and pestle.
1 Porcelain evaporating dish.
1 Triangle.
1 Rubber stopper fitting a test tube with a bent delivery tube for generation of H_2S.

LIST OF REAGENTS.

SIZE OF BOTTLE.	LABEL.	STRENGTH OF SOLUTION.
8 oz	Con. H_2SO_4	Commercial.
8 "	Dil. H_2SO_4	1—8 C. P.
8 "	Con. HNO_3	.. C. P.
8 "	Dil. HNO_3	1—2 C. P.
8 "	Con. HCl	.. C. P.
8 "	Dil. HCl	1—4 C. P.
8 "	NH_4HO	.. C. P.
8 "	NaHO	1—5
8 "	Na_2CO_3	1—3
4 "	NH_4Cl	1—10
4 "	$(NH_4)_2CO_3$	1—10
4 "	$(NH_4)_2C_2O_4$	1—24
4 "	$(NH_4)_2S$	..
4 "	$HC_2H_3O_2$	Commercial.
4 "	Na_2HPO_4	1—10
4 "	$BaCl_2$	1—10
4 "	$Ba(NO_3)_2$	1—12
4 "	$CaSO_4$	Saturated Sol.
4 "	$CaCl_2$	1—10
4 "	$MgSO_4$	1—10
4 "	Fe_2Cl_6	1—20
4 "	K_4FeCy_6	1—10
4 "	K_3FeCy_6	1—20
4 "	$K_2Cr_2O_7$	1—10
4 "	$Pb(C_2H_3O_2)_2$	1—10
1 "	$PtCl_4$	1—20
1 "	$AgNO_3$	1—20
1 "	$Co(NO_3)_2$	1—20
1 "	$HgCl_2$	1—20

DRY CHEMICALS.

1 oz	Na_2CO_3	
1 "	$NaC_2H_3O_2$	
1 "	$Na_2B_4O_7$	
1 "	KNO_3	
1 "	FeS	
1 "	$H_2C_4H_4O_6$	

TABLE I.

QUANTIVALENCE OF ELEMENTS.

	MONADS	DYADS.	TRIADS.	TETRADS:
Non-Metals.	H	O	N	C
	Cl	S	P	Si
	Br		B	
	I	Ca	As	Al
	F	Ba		Cr
		Sr	Sb	Fe
	K	Mg	Bi	(as ferric)
	Na	Fe	Au	Pt
	NH_4	(as ferrous)		(as platinic)
	Ag	Zn		Sn
		Mn		(as stannic)
		Co		
		Ni		
		Pb		
		Hg		
		Cu		
		Cd		
		Pt		
		(as platinous)		
		Sn		
		(as stannous)		

TABLE II.

BASICITY OF ACIDS.

MONOBASIC	DIBASIC.	TRIBASIC.	TETRABASIC.
HCl	H_2S	H_3PO_4	$H_4P_2O_7$
HBr	H_2CO_3	H_3AsO_4	H_4SiO_4
HI	H_2SO_4	H_3AsO_3	H_4FeCy_6
HF	H_2SO_3	H_3FeCy_6	
HCy	$H_2S_2O_3$	H_3BO_3	
HNO_3	$H_2C_2O_4$		
HNO_2	$H_2C_4H_4O_6$		
$HClO_3$			
$HC_2H_3O_2$			
$HCyS$			

GROUP I.

METALS OF THE ALKALIES.

Potassium	$K=39.1$.
Sodium	$Na=23$.
Ammonium	$NH_4=18$

POTASSIUM.

1. To a solution of any salt of potassium in a porcelain dish, add $PtCl_4$ and a few drops of HCl and evaporate to dryness on a water bath. Then add a little H_2O and a yellow crystalline precipitate of the double chloride of potassium and platinum $2KCl. PtC_4$ will remain.

If the potassium salt is KCl the HCl may be omitted.

2. To a solution of a salt of potassium in a test tube add a little $NaHO$, then add a strong solution of tartaric acid $H_2C_4H_4O_6$ *to an acid reaction*, and a white crystalline precipitate of potassium hydrogen tartartrate $KHC_4H_4O_6$ will be found.

If the potassium compound be KHO or K_2CO_3 the $NaHO$ may be omitted.

If the solution is dilute and warm, the precipitate will not be formed immediately, and if very dilute will not be formed at all. Violent shaking aids the precipitation.

3. Compounds of potassium, when introduced into the flame of a Bunsen burner, on a platinum wire, especially after being moistened with HCl, color the same violet (*characteristic test*).

4. In the spectrum this flame reveals two characteristic lines, one bright line in the red and a fainter one in the violet portion of the spectrum (*characteristic test*).

SODIUM.

5. All compounds of sodium, when introduced into the flame of a Bunsen burner, color the same *intensely yellow* (*characteristic test*).

6. The spectrum of sodium consists of one bright yellow line near the center of the spectrum (*characteristic test*).

AMMONIUM.

7. Place a small quantity of a solution of any salt of ammonium, or of the solid salt with a few drops of H_2O, into a porcelain mortar and triturate thoroughly with CaH_2O_2, and NH_3 will be evolved, which may be recognized by its characteristic *odor;* by the vapor turning reddened litmus paper *blue;* and by forming *white fumes,* when an object moistened with a volatile acid (HCl, HNO_3, $HC_2H_3O_2$) is brought near the mixture (*characteristic test*).

These white fumes are caused by the production of solid salts of ammonium formed by the combination of the gases.

8. Put into a test tube some solid salt of ammonium or a solution, add NaHO and boil; NH_3 will be evolved, which may be determined by the reactions mentioned in 7 (*characteristic test.*)

9. To a solution of any salt of ammonium in a porcelain dish add $PtCl_4$ and a few drops of HCl, and evaporate to dryness on a water bath. On the addition of a little H_2O a yellow crystalline precipitate of $2NH_4ClPtCl_4$ will remain, which resembles in its physical properties the corresponding potassium compound.

10. To a solution of a salt of ammonium add a little NaHO, then a strong solution of $H_2C_4H_4O_6$ to an *acid reaction,* and a white crystalline precipitate of $NH_4HC_4H_4O_6$ will be produced. In case NH_3 or $(NH_4)_2CO_3$ is employed in making this test the NaHO may be omitted.

In dilute and warm solutions this precipitate is formed only on standing for some time, and if the solutions are too dilute no precipitate whatever occurs.

SCHEME I.

TESTING FOR METALS OF GROUP I.

1. With a portion of the substance test for ammonium according to 7 or 8.

NOTE: It is necessary to test for ammonium first, since a contamination of sodium or the faint violet color produced by ammonium salts in the flame may mislead the beginner.

2. Test for potassium according to 3 and 4.
3. Test for sodium according to 5 and 6.

SEPARATION OF GROUP I.

1. Evaporate the solution containing a mixture of this group to dryness in a porcelain crucible, and ignite till no more fumes are given off.

Volatilized .... NH_4

2. Dissolve residue in a little water, transfer to a porcelain dish, add excess of $PtCl_4$ and a little HCl, and evaporate to dryness on a water bath. Then add a little water and filter.

Filter contains .... K
Solution .... Na

GROUP II. $(NH_4)_2CO_3$ GROUP.

METALS OF THE ALKALINE EARTHS.

Barium	Ba=137
Strontium	Sr=87.6
Calcium	Ca=40
Magnesium	Mg=24

NOTE: Ammonium carbonate $(NH_4)_2CO_3$ precipitates all the metals of this group, and is called the *group* reagent. The precipitation of magnesium is prevented by the presence of ammonium chloride.

BARIUM.

11. To a solution of a barium salt in a test tube add ammonium carbonate $(NH_4)_2CO_3$, and a white precipitate of *barium carbonate* $BaCO_3$ will be formed. The other alkaline carbonates deport themselves in a similar manner with barium salts.

12. To a solution of a barium salt add ammonium oxalate $(NH_4)_2C_2O_4$, and a white precipitate of *barium oxalate* BaC_2O_4 will be produced, which is soluble in HNO_3 and HCl.

13. To a solution of any salt of barium add $H_2\,SO_4$, and a white precipitate of *barium sulphate* $BaSO_4$ will be formed.

14. To a solution of a barium salt add potassium dichromate $K_2Cr_2O_7$, and a yellow precipitate of *barium chromate* $BaCrO_7$ will be formed, which is soluble in HNO_3 and in HCl.

15. To a solution of a barium salt add sodium hydrogen phosphate Na_2HPO_4, and a white precipitate of *barium hydrogen phosphate* $BaHPO_4$ will be produced, soluble in acids.

16. The compounds of barium, when introduced into the flame of a Bunsen burner, especially after being moistened with HCl, impart to it a *yellowish green* color (*characteristic test*).

17. The spectrum of the barium flame reveals a series of bright lines in the green, one bright line in the yellow and fainter ones in the orange (*characteristic test*).

STRONTIUM.

18. To a solution of a strontium salt add $(NH_4)_2CO_3$, and a white precipitate of $SrCO_3$ will result. In the place of $(NH_4)_2CO_3$ any other alkaline carbonate may be employed.

19. To a solution of a strontium salt add $(NH_4)_2C_2O_4$

and a white precipitate of SrC_2O_4 will be formed, which is soluble in HNO_3 and HCl.

20. To a solution of a salt of strontium add dil. H_2SO_4 or any soluble sulphate as Mg SO_4, and a white precipitate of $SrSO_4$ will be produced.

NOTE: Strontium salts are evidently not precipitated by a saturated solution of $SrSO_4$—*distinction from barium.* A saturated solution of calcium sulphate Ca SO_4 precipitates solutions of strontium salts only after a little time —*distinction from barium.*

21 To a solution of a salt of strontium add Na_2HPO_4, and a white precipitate of $SrHPO_4$ will be formed, soluble in acids.

22. Strontium salts, especially after being moistened with HCl, impart to the *flame* a crimson color (*characteristic test*).

23. The spectrum of the strontium flame shows a series of bright lines in the red and orange and one bright line in the blue (*characteristic test*).

CALCIUM.

24. To a solution of a calcium salt add $(NH_4)_2CO_3$, or any other alkaline carbonate, and a white precipitate of calcium carbonate Ca Co_3 will be formed.

25. To a solution of a calcium salt add $(NH_4)_2C_2O_4$ and a white precipitate of CaC_2O_4 will be formed, which is soluble in HNO_3 and HCl.

26. To a solution of a calcium salt—not too dilute—add dil. H_2SO_4 or a soluble sulphate as $MgSO_4$, and a white precipitate of $CaSO_4$ will be produced.

NOTE: Salts of calcium are evidently not precipitated by a saturated solution of $CaSO_4$—*distinction from barium and strontium.*

27. To a solution of a calcium salt add Na_2HPO_4, and

a white precipitate of $CaHPO_4$ will be produced, which is soluble in acids.

28. Calcium salts especially after being moistened with HCl color the *flame* yellowish red (*characteristic test*].

29. The spectrum of the calcium flame reveals, besides some faint lines in the orange, yellow and violet, one bright orange line just to the left, and one bright green line just to the right of the sodium line [*characteristic test*].

MAGNESIUM.

30. To a solution of a magnesium salt—not too dilute—add $(NH_4]_2CO_3$, and a white precipitate of $[NH_4]_2 Mg2CO_3$ will be formed. It may require some time before the precipitate separates. NH_4Cl prevents the precipitation except in highly concentrated solutions.

31. To a solution of a magnesium salt add Na_2CO_3, and a white precipitate of *basic magnesium carbonate* $4MgCO_3+Mg[HO]_2$ will be produced. NH_4Cl prevents the formation of this precipitate.

32. To a solution of a magnesium salt add sodium hydroxide NaHO, and a white precipitate of magnesium hydroxide $Mg[HO]_2$ will be formed.

33. To a solution of a magnesium salt add NH_4HO, and one-half of the magnesium will be precipitated as $Mg[HO]_2$, while the other half remains in solution in the form of an ammonium magnesium salt.

34. To a solution of a magnesium salt add Na_2HPO_4, and a white precipitate of $MgHPO_4$ will be formed, which is soluble in free acids.

35. To a solution of a magnesium salt add NH_4Cl, NH_4HO and $(NH_4)_2CO_3$—no precipitate will be formed—then add Na_2HPO_4, and a white precipitate of magnesium ammonium phosphate $MgNH_4PO_4$ will be produced (*characteristic test*).

SCHEME II.

TESTING FOR METALS OF GROUP II.

1. Test for barium according to 16 and 17.
2. “ “ strontium “ “ 22 and 23.
3. “ “ calcium “ “ 28 and 29.
4. “ “ magnesium “ “ 35

SEPARATION OF GROUP II.

1. To a solution of this group add NH_4Cl,NH_4HO and finally $(NH_4)_2CO_3$ in excess, i. e.: until the farther addition of $(NH_4)_2CO_3$ no longer produces a precipitate, then heat to boiling and filter.

Solution contains........................Mg.

The presence of Mg. may be verified by the addition of Na_2HPO_4 (see 35).

2. Dissolve the above precipitate consisting of $BaCO_3$, $SrCO_3$ and $CaCO_3$ by adding *acetic acid* $HC_2H_3O_2$ to the filter, dilute with H_2O and finally add potassium dichromate $K_2Cr_2O_7$ in excess and filter.

Filter contains..........................Ba.

3. To the filtrate obtained above add $(NH_4)_2CO_3$ in excess, heat to boiling and filter. Reject filtrate. Dissolve the precipitate in the smallest possible quantity of $HC_2H_3O_2$ and to the solution add a sufficient quantity (2 or 3 oz.) of a solution of potassium sulphate K_2SO_4 (1:200). Allow to stand 24 hours and filter.

Filter contains..........................Sr

Solution ....Ca

Note: By employing a solution of K_2SO_4 of the above strength there will be no danger of precipitating any of the calcium as $CaSO_4$.

GROUP III. $(NH_4)_2S$ GROUP.

METALS, WHOSE SULPHIDES ARE SOLUBLE IN DILUTE ACIDS BUT INSOLUBLE IN WATER.

Zinc	$Zn = 65.$
Aluminum	$Al = 27.4.$
Manganese	$Mn = 55.$
Iron	$Fe = 56.$
Cobalt	$Co = 58.8.$
Nickel	$Ni = 58.8.$
Chrominum	$Cr = 52.5.$

NOTE: All the above metals are precipitated from neutral or alkaline solutions by *ammonium sulphide* $(NH_4)_2S$, and consequently are separated by this means from Groups I and II. Aluminum and chromium are precipitated as hydroxides.

ZINC.

36. To a solution of a zinc salt add $(NH_4)_2S$, and a white precipitate of *zinc sulphide* ZnS will be produced.

37. To a solution of a zinc salt cautiously add any alkaline hydroxide as $NaHO$ or NH_4HO, and a *white* gelatinous precipitate of *zinc hydroxide* $Zn(HO)_2$ will be formed. This precipitate re-dissolves completely on adding an excess of the precipitant.

38. To a solution of a zinc salt add Na_2CO_3, and a white precipitate of *basic carbonate of zinc* $3Zn(HO)_2 2ZnCO_3$ will be produced.

39. Moisten a small quantity of any compound of zinc on charcoal with a solution of $Co2NO_3$, and heat before the blowpipe, and the mass will assume a beautiful green color on cooling (*characteristic test*). The green mass is a compound of the two oxides of zinc and cobalt [Rinman's green].

ALUMINUM.

40. To a solution of any salt of aluminum add $[NH_4]_2S$, and a white gelatinous precipitate of *aluminum hydroxide* $Al_2[HO]_6$ will be formed, while at the same time H_2S is evolved.

41. To a solution of a salt of aluminum add a fixed alkaline hydroxide as NaHO and $Al_2[HO]_6$ will be precipitated, which is readily soluble in an excess of reagent.

42. To a solution of a salt of aluminum add NH_4HO, and $Al_2[HO]_6$ will be precipitated, which is difficultly soluble in a large excess of the reagent.

43. To a solution of a salt of aluminum add Na_2CO_3, and $Al_2[HO]_6$ will be formed with evolution of CO_2.

44. Ignite on charcoal before the blowpipe alumina or any compound of aluminum, then moisten with a solution of $Co2NO_3$ and again ignite, and a beautiful blue mass will be obtained [*characteristic test*]. This blue mass is a combination of the two oxides of aluminum and cobalt (Thenard's blue].

MANGANESE.

NOTE: In the ordinary course of analysis manganese is always in the form of manganous salts.

The black manganese dioxide MnO_2, the brown manganic oxide Mn_2O_3 and the red manganous manganic oxide Mn_3O_4 all dissolve in hot HCl to *manganous chloride* $MnCl_2$ with the evolution of *chlorine gas.*

45. To a solution of a manganous salt add $[NH_4]_2S$, and a light, flesh-colored precipitate of *manganous sulphide* MnS will be formed.

46. To a solution of a manganous salt add any alkaline hydroxide as NaHO or NH_4HO, and a whitish precipitate of *manganous hydroxide* $Mn[HO]_2$ will be formed. This precipitate rapidly assumes a brown color owing to

the absorption of oxygen from the air and the formation of manganic hydroxide.

47. To a solution of a manganous salt add Na_2CO_3, and a white precipitate of *manganous carbonate* $MnCO_3$ will be produced. Like the hydroxide this precipitate rapidly turns brown on exposure to the air.

48. Heat to fusion on a platinum foil a small quantity of any compound of manganese with some dry alkaline carbonate as Na_2CO_3 and an oxidizing agent as KNO_3, and the fused mass will assume a *bright green color* [*characteristic test*]. The green color is due to the oxidation of the manganese to sodium manganate Na_2MNO_4.

49. Compounds of manganese form with *borax* in the outer or oxidizing flame of the blowpipe a bead, which is *violet* while hot and *amethyst-red* when cold [*characteristic test*]. If the bead is highly saturated with manganese it appears black.

NOTE: To make the borax bead, bend a small loop at the end of a platinum wire, heat it to redness and while hot plunge it into some pulverized borax. Enough borax for the purpose will readily adhere to the wire. Heat the borax before the blowpipe or in the flame of a Bunsen burner until it fuses quietly, when a clear, colorless bead should be obtained. With the hot bead take up a minute quantity of the substance to be tested, and heat in the oxidizing or reducing flame as directed, until it is completely dissolved. If the color of the bead is too light, add a fresh portion of the substance and fuse again. The substance to be tested should be either in the form of a powder or a precipitate.

IRON.

NOTE: Iron is met with in the course of analysis in two distinct series of compounds, viz.:

1. Ferrous compounds, and
2. Ferric compounds.

Ferrous compounds are converted into ferric compounds by exposure to the air, or more rapidly by oxydizing agents as HNO_3, Cl, Br. &c.

Ferric compounds are converted into ferrous compounds by reducing agents as H_2S, $(NH_4)_2S$, &c.

Hence if iron is found in the course of analysis, the original substance must be employed to determine whether it exists in the ferrous or ferric condition or both.

FERROUS COMPOUNDS.

50. To a solution of a ferrous salt add $(NH_4)_2S$, and a *black* precipitate of *ferrous sulphide* FeS will be formed.

51. To a solution of a ferrous salt add any alkaline hydroxide as NaHO or NH_4HO, and a *white* precipitate of *ferrous hydroxide* $Fe(HO)_2$ will be formed. This precipitate rapidly absorbs oxygen from the air and assumes a greenish and finally a reddish brown color. If the solution of the ferrous salt itself has undergone partial oxidation the precipitate will of course be discolored when formed.

52. To a solution of a ferrous salt add potassium ferrocyanide, and a *light blue* precipitate of *potassium ferrous ferrocyanide* K_2FeCfy will be formed, which on exposure to the air or more rapidly by the action of oxidizing agents converted into the *dark blue ferric ferrocyanide*. Fe_4Cfy_3 (Prussian blue).

53. To a solution of a ferrous salt add potassium ferricyanide K_3Cfy, and a *dark blue* precipitate of *ferrous ferricyanide* Fe_3Cfy_2 will be produced (*characteristic test*).

In color this precipitate can not be distinguished from Prussian blue.

54. Borax dissolves all compounds of iron in the oxi-

dizing flame forming beads, which according to the degree of saturation are *yellow* to *dark red* while hot, and *colorless* to *reddish yellow* when cold. In the reducing flame these beads become *colorless* or, when strongly saturated, *bottle green* owing to the reduction of the ferric oxide to ferrous oxide.

FERRIC COMPOUNDS.

55. To a solution of a ferric salt add $(NH_4)_2S$ and a *black* precipitate of *ferrous sulphide* FeS will be formed mixed with free sulphur.

56. To a solution of a ferric salt add any alkaline hydroxide as NaHO or NH_4HO, and a *reddish brown* precipitate of *ferric hydroxide* $Fe_2(HO)_6$ will be produced.

57. To a solution of a ferric salt add K_4Cfy, and a *dark blue* precipitate of *ferric ferrocyanide* Fe_4Cfy_3 (Prussian blue) will be produced (*characteristic test*).

58. To a solution of a ferric salt add a soluble sulphocyanide as KCyS, and a blood-red *coloration* will be produced, owing to the formation of *ferric sulphocyanide* $Fe_2(CyS)_6$ (*characteristic test*). The color is destroyed by the addition of mercuric chloride, as well as of phosphates, acetates, oxalates, tartrates, borates, or their corresponding acids.

59. With borax beads ferric compounds behave just as ferrous compounds (See 54).

COBALT.

60. To a solution of a cobalt salt add $(NH_4)_2S$, and a *black* precipitate of *cobalt sulphide* CoS will be formed. This precipitate is almost insoluble in acetic acid and in dilute HCl; but readily soluble in HNO_3 and in nitrohydrochloric acid.

61. To a solution of a cobalt salt add a fixed alkaline hydroxide as NaHO, and a blue basic salt of cobalt will

be formed, which on boiling is changed to the pale red *cobalt hydroxide* $Co(HO)_2$. This precipitate is usually more or less discolored, owing to absorption of oxygen from the air and the formation of a higher oxide of cobalt.

62. To a solution of a cobalt salt add NH_4HO, and $Co(HO)_2$ will be produced. This precipitate is soluble in excess of ammonia forming a reddish-brown solution. Solutions containing free acids are not precipitated by NH_4HO owing to the solubility of cobalt hydroxide in ammonium salts.

63. To a solution of a cobalt salt add *potassium nitrite* KNO_2 in excess, then add acetic acid till the precipitate first formed is re-dissolved and the solution is strongly acid; heat gently, and a yellow crystalline precipitate of *potassium cobaltic nitrite* $6KNO_2$, $Co_2O_3(N_2O_3)_2$ will be formed. In very dilute solutions the precipitate separates only after some time.

64. With *borax* compounds of cobalt form beautiful blue beads both in the outer and inner flame of the blow pipe (*characteristic test*).

NICKEL.

65. To a solution of a salt of nickel add $(NH_4)_2S$, and a *black* precipitate of *nickel sulphide* NiS will be produced. This compound is slightly soluble in $(NH_4)_2S$, especially if free ammonia is present, and hence the liquid from which the NiS separates is usually colored brownish. NiS is insoluble in acetic acid and in dilute HCl; but readily soluble in HNO_3 and in nitro-hydrochloric acid.

66. To a solution of a nickel salt add a fixed alkaline hydroxide as NaHO, and an *apple green* precipitate of nickel hydroxide $Ni(HO)_2$ will be formed.

67. To a solution of a nickel salt add NH_4HO carefully, and a slight precipitate of $Ni(HO)_2$ will be formed, which

readily dissolves on a farther addition of ammonia forming a blue solution.

68. *Borax* dissolves compounds of nickel in the oxidizing flame forming a clear bead which is *violet* while hot, and reddish-brown when cold. When held in the reducing flame this bead becomes gray and opake, owing to the reduction of the nickel oxide to metallic nickel (*characteristic test*).

CHROMIUM.

NOTE: This metal forms two series of compounds, in one of which, the *chromic compounds*, it constitutes the *base*, and in the other, the *chromates*, it constitutes the acid.

Oxidizing agents as Cl, Br, KNO_3, &c., under the proper conditions, readily convert chromic compounds into chromates. Reducing agents as H_2S,H_2SO_3,&c., especially in acid solution, rapidly change chromates into chromic compounds. Hence in the ordinary course of analysis, even when this metal occurs in the form of chromic acid or chromates, it will always be found as a base in the $(NH_4)_2S$ group.

69. To a solution of a chromic salt add $(NH_4)_2S$ and a greenish precipitate of *chromium hydroxide* $Cr_2(HO)_6$ will be formed, while at the same time H_2S is evolved.

70. To a solution of a chromic salt add a fixed alkaline hydroxide as NaHO, and $Cr_2(HO)_6$ will be precipitated which readily dissolves in an excess of the reagent in the cold forming a green solution, and is reprecipitated on boiling.

71. To a solution of a chromic salt add NH_4HO, and $Cr_2(HO)_6$ will be precipitated, which is only slightly soluable in excess of ammonia and imparts to the supernatant liquid a pink-red color. On boiling the precipitation is complete.

72. Heat to fusion on a platinum foil a small quantity of a chromic compound with Na_2CO_3 and KNO_3, and the fused mass will acquire a *yellow* color owing to the production of the yellow *sodium chromate* Na_2CrO_4 (*characteristic test*). The presence of chromic acid may be confirmed by dissolving the fused mass in water, acidifying with acetic acid $HC_2H_3O_2$ and adding lead acetate $Pb(C_2H_3O_2)_2$, when a yellow precipitate of *lead chromate* $PbCrO_4$ will be formed.

73. *Borax* dissolves all compounds of chromium both in the oxidizing and the reducing flame of the blowpipe, forming beads, which are *yellowish-green*, while hot and *emerald-green* when cold (*characteristic test*).

SCHEME III.

TESTING FOR METALS OF GROUP III.

Reserve a small portion of the substance for *dry tests* and dissolve the remainder in HCl, if it is not soluble in H_2O. To a portion of the solution add NH_4HO and $(NH_4)_2S$; the precipitate is either *black* or *light.*

BLACK.

FeS	Test original solution for ferrous salts with K_3Cfy (53).
	Test original solution for ferric salts with K_4Cfy (57).
CoS	Blue borax bead (64).
NiS	Brown borax bead (68).

LIGHT.

$Al_2(HO)_6$ white	Blue mass on charcoal with $Co(NO_3)_2$ (44).
Zn S white	Green mass on charcoal with $Co(NO_3)_2$ (39).
$Cr_2(HO)_6$ green	Green borax bead (73) or yellow mass on platinum foil with Na_2CO_3 and KM_3NO (72).
MnS flesh-colored	Amethyst red bead (49) or green mass on platinum foil with Na_2CO_3 and KNO_3 (48).

SEPARATION OF GROUP III.

1.—To a solution of the metals of this group add NH_4HO and $(NH_4)_2S$ in excess, filter and wash. Reject filtrate. Perforate the filter with a glass rod, and wash the precipitate into a beaker; then add dilute HCl in excess and filter—*preserve filtrate* (A). Wash the black residue of CoS and NiS on filter once or twice with H_2O—reject washings. Perforate the filter, wash residue into a porcelain dish, add concentrated HNO_3 and evaporate to dryness on a water bath. Dissolve residue in a little H_2O, add KNO_2 freely, and then $HC_2H_3O_2$ to a *strongly acid reaction.* Warm gently, allow to stand 24 hours and filter.

Filter contains Co.	*Filtrate contains Ni.*
The precipitate on filter is bright yellow. Confirm presence of cobalt by bead test (64).	Confirm presence of nickel by adding NaHO, which gives the characteristic apple-green precipitate of $Ni(HO)_2$.

2.—To the filtrate (A) add Na_2CO_3 till, after stirring thoroughly, a slight precipitate remains, then add 8 or

10 drops of bromine and heat on a sand bath, at the same time keeping the solution neutral by frequent additions of Na_2CO_3 in small quantities. Finally add Na_2CO_3 in excess, boil for a few minutes to expel the last traces of bromine and filter.

Filtrate contains Cr. in the form of Na_2CrO_4, coloring the solution yellow. Confirm by acidifying with $HC_2H_3O_2$ and adding $Pb(C_2H_3O_2)_2$ which yields the yellow precipitate of $PbCrO_4$.	*Precipitate* (B) on filter contains Fe, Al, Mn and Zn.

3.—Wash the precipitate (B) into a beaker, add Con. HCl and heat until the precipitate is entirely dissolved, dilute with water, add Na_2CO_3 until a slight precipitate remains, then a few drops of $HC_2H_3O_2$ and finally $NaC_2H_3O_2$ in excess. Heat to boiling and filter while hot.

Precipitate (C) on filter contains Fe and Al.	*Filtrate* (D) contains Mn and Zn.

4.—Dissolve precipitate (C) in HCl, add Na_2CO_3 until the free acid is neutralized, i. e.: until the solution just begins to turn yellow, then add sodium thiosulphite $Na_2S_2O_3$ in excess, allow the solution to become colorless, boil for half an hour or more and filter.

Filter contains Al. Confirm presence of Al by heating on charcoal with $Co(NO_3)_2$(44).	*Filtrate contains* Fe. Confirm presence of iron by adding $(NH_4)_2S$.

NOTE: If on the addition of the $Na_2S_2O_3$ the solution does not become colorless in a few minutes, or if the precipitate is brown (Fe_2O_3) instead of white (Al_2O_3), then too much Na_2CO_3 has been added. A few drops of HCl will remedy the difficulty.

5.—To filtrate (D) add a few drops of bromine, heat to boiling and filter.

Filter contains Mn.	Filtrate contains Zn.
Confirm presence of Mn on platinum foil with Na_2CO_3 and KNO_3 (48) or by the bead test.	Confirm the presence of Zn by adding $(NH_4)_2S$, which will precipitate white ZnS. This precipitate may be tested farther on charcoal with $Co(NO_3)_2$ (39).

GROUP IV. H_2S GROUP.

METALS, WHOSE SULPHIDES ARE INSOLUBLE IN DILUTE ACIDS, AND HENCE ARE PRECIPITATED FROM ACID SOLUTIONS BY HYDROSULPHURIC ACID H_2S.

Silver	Ag=108.
Lead	Pb=207.
Mercury	Hg=200.
Copper	Cu=63.4.
Cadmium	Cd=112.
Bismuth	Bi=210.
Arsenic	As=75.
Antimony	Sb=122.
Tin	Sn=118.

SILVER.

74. To a solution of a salt of silver add H_2S and a *black* precipitate of *silver sulphide* Ag_2S will be formed, which is insoluble in $(NH_4)_2S$, but soluble in boiling HNO_3.

75. To a solution of a silver salt add a fixed alkaline hydroxide as NaHO, and a *light brown* precipitate of *silver oxide* Ag_2O will be produced.

76. To a solution of a silver salt add NH_4HO in *small*

quantity, and Ag_2O will be precipitated, which readily dissolves on farther addition of the precipitant.

77. To a solution of a silver salt add HCl or any soluble chloride, and a *white* precipitate of *silver chloride* AgCl will be produced, which is insoluble in acids, but soluble in NH_4HO (*characteristic test*).

78. Heat before the blowpipe on charcoal with Na_2CO_3 any compound of silver, and *bright malleable* globules of metallic silver will be obtained (*characteristic test*).

LEAD.

79. To a solution of a lead salt add H_2S, and a *black* precipitate of *lead sulphide* PbS will be formed, which is insoluble in $(NH_4)_2S$, but soluble in boiling HNO_3. In the presence of much HCl the precipitate may at first be *red*, consisting of PbS and $PbCl_2$; but an excess of H_2S converts the whole into black PbS.

80. To a solution of a lead salt add a fixed alkaline hydroxide as Na HO, and a *white* precipitate of *lead hydroxide* $Pb(HO)_2$ will be formed, which is soluble in excess of the precipitant.

81. To a solution of a lead salt add NH_4HO, and $Pb(HO)_2$ will be formed, insoluble in excess of the reagent.

82. To a solution of lead salt, not too dilute, add HCl or a soluble chloride, and a *white* precipitate of lead chloride Pb Cl_2 will be produced, which is soluble in hot water.

83. To a solution of a lead salt add H_2SO_4 or a soluble sulphate, and a *white* precipitate of *lead sulphate* Pb SO_4 will be formed, slightly soluble in strong HNO_3.

84. To a solution of a lead salt add $K_2Cr_2O_7$, and a *yellow* precipitate of *lead chromate* $PbCrO_4$ will be produced, which is soluble in excess of NaHO (*characteristic test*).

85. Heat before the blowpipe on charcoal with Na_2CO_3 any compound of lead, and soft, malleable globules of metallic lead will be obtained (*characteristic test*).

MERCURY.

Murçury forms two distinct series of compounds, the *mercurous* compounds and the *mercuric* compounds.

MERCUROUS COMPOUNDS.

86. To a solution of mercurous salt and H_2S, and a black precipitate of *mercurous sulphide* Hg_2S will be produced, which is insoluble in $(NH_4)_2S$, as well as in boiling HNO_3, but readily soluble in nitro-hydrochloric acid.

87. To a solution of a mercurous salt add an alkaline hydroxide as NaHO or NH_4HO, and a *black* precipitate of *mercurous oxide* Hg_2O will be formed.

88. To a solution of mercurous salt add HCl or any soluble chloride, and a *white* precipitate of *mercurous chloride* Hg_2Cl_2 will be formed. This precipitate turns *black* when treated with ammonia, but does not dissolve (*characteristic test*).

89. Introduce into a neutral or slightly acid solution of a mercurous salt a clean wire or strip of copper, and in a few minutes the copper will be covered with a coating of metallic mercury, which on being rubbed with a piece of paper or cloth, will assume a silver-white luster. On heating the copper, the mercury will be volatilized and the coating destroyed.

MERCURIC COMPOUNDS.

90. To a solution of a mercuric salt add H_2S, and at first a white precipitate will be formed, which on farther addition of the reagent changes to yellow, then through orange to reddish-brown, and finally when H_2S is added in excess it is converted into the *black mercuric sulphide* HgS. This precipitate is insoluble in $(NH_4)_2S$ as well as

in hot HNO_3, but is readily dissolved in nitro-hydrochloric acid. The gradual change of color produced by H_2S is characteristic of mercuric salts.

91. To a solution of a mercuric salt add a fixed alkaline hydroxide as NaHO, and a *yellow* precipitate of *mercuric oxide* HgO will be produced.

92. To a solution of a mercuric salt add NH_4HO, and a *white* precipitate will be formed. In the case of mercuric chloride $Hg\,Cl_2$, this white precipitate is *mercurammonium* chloride $(NH_2Hg)Cl$.

93. To a solution of a mercuric salt add stannous chloride $Sn\,Cl_2$, and a *white* precipitate of *mercurous chloride* Hg_2Cl_2 will at first be formed. On farther addition of the reagent the precipitate turns grey, owing to the separation of metallic mercury.

94. Acidulate a solution of a mercuric salt with HCl and apply the test with copper as described for mercurous salts, and the same result will be obtained (see 89) (*characteristic test*).

COPPER.

95. To a solution of a copper salt add H_2S, and a *black* precipitate of *copper sulphide* CuS will be produced, which is insoluble in $(NH_4)_2S$, but readily soluble in hot HNO_3.

96. To a solution of a copper salt add a fixed alkaline hydroxide as NaHO, and a *light blue* precipitate of *copper hydroxide* CuH_2O_2 will be produced, which on application of heat turns black, owing to the production of copper oxide CuO.

97. To a solution of a copper salt add NH_4HO in small quantity, and CuH_2O_2 will be precipitated. On the addition of NH_4HO in excess the precipitate dissolves, forming a deep blue solution (*characteristic test*).

98. Into a slightly acid solution of a copper salt in-

troduce a clean piece of iron or steel, and in a few minutes it will receive a red coating of metallic copper (*characteristic test*).

99. Metallic copper or any compound of copper moistened with HCl, and held in the flame of a Bunsen burner or a blowpipe, imparts to the flame an emerald green color (*characteristic test*).

100. The *borax* beads produced by compounds of copper in the oxidizing flame of the blowpipe are *green* while hot and *blue* when cold (*characteriststic test*).

CADMIUM.

101. To a solution of a cadmium salt add H_2S, and a *bright yellow* precipitate of *cadmium sulphide* CdS will be formed, insoluble in $(NH_4)_2S$ (*characteristic test*), but soluble in HNO_3.

102. To a solution of a cadmium salt add NH_4HO in small quantity, and a white precipitate of cadmium hydroxide CdH_2O_2 will be formed, which is readily soluble in excess of the reagent, forming a colorless solution.

BISMUTH.

103. To a solution of a bismuth salt add H_2S and a *black* precipitate of *bismuth sulphide* Bi_2S_3 will be formed, which is insoluble in $(NH_4)_2S$, but soluble in hot HNO_3.

104. To a solution of a bismuth salt add an alkaline hydroxide as $NaHO$ or NH_4HO and a *white* precipite of *bismuth hydroxide* $Bi(HO)_3$ will be produced.

105. To a solution of a bismuth salt add $K_2Cr_2O_7$, and a *yellow* precipitate of *basic bismuth chromate* $Bi_2O(CrO_4)_2$ will be formed, which is soluble in dilute HNO_3 and is distinguished from $PbCrO_4$ in being insoluble in excess of a fixed alkaline hydroxide as $NaHO$.

106. To a solution of a bismuth salt containing not

too much free acid, add a large quantity of water, and a white precipitate of a basic salt of bismuth will be formed (*characteristic test*) In the case of bismuth chloride $BiCl_3$ this precipitate is *bismuth oxychloride* $BiOCl$. Bismuth nitrate $Bi(NO_3)_3$ yields *basic nitrate* of *bismuth* $BiONO_3$. These precipitates are readily soluble on addition of HCl or HNO_3, and are distinguished from the corresponding *antimony* precipitates by being insoluble in *tartaric acid.*

NOTE : If a small quantity of bismuth is present in a large excess of free acid, the latter, which would prevent the above mentioned reaction, must be removed, before the test is applied. In the case of HCl or HNO_3 this is best accomplished by evaporating the solution on a water bath to a few drops. If the acid is H_2SO_4, precipitate the bismuth as $Bi(HO)_3$ with NH_4HO, and either filter or allow the precipitate to subside and decant the supernatant liquid; then dissolve the precipitate in the smallest possible quantity of HCl, and the solution will be ready for the application of the test.

107. Heat before the blowpipe on charcoal with Na_2CO_3 any compound of bismuth, and easily fusible globules of metallic bismuth will be obtained. These globules are distinguished from lead in being *brittle*, and from antimony by a *yellow* incrustation of Bi_2O_3 on the charcoal and by the *absence* of heavy white fumes (*characteristic test*).

ARSENIC.

Arsenic forms two oxides, arsenic trioxide As_2O_3, the anhydride of *arsenious* acid H_3AsO_3, and arsenic pentoxide As_2O_5, the anhydride of *arsenic* acid H_3AsO_4. Both of these acids and their combinations, however, are precipitated by H_2S in acid solutions, and hence for the sake of convenience arsenic is classed among the bases.

ARSENIOUS COMPOUNDS.

108. Dissolve a small quantity of As_2O_3 in dilute HCl and to the solution add H_2S, and a bright *yellow* precipitate of *arsenic trisulphide* As_2S_3 will be formed, which is soluble in $(NH_4)_2S$, as well as in boiling HNO_3.

109. Dissolve some As_2O_3 in water containing a small quantity of NaHO, and a solution of *sodium arsenite* Na_3AsO_3 will be formed. To a portion of this solution add $AgNO_3$, and a *yellow* precipitate of *silver arsenite* Ag_3AsO_3 will be formed. This precipitate is readily soluble in dilute acids, as well as in NH_4HO (*distinction from* As_2O_5).

110. To another portion of the sodium arsenite solution obtained above add a solution of copper sulphate $CuSO_4$, and a *yellowish green* precipitate of copper hydrogen arsenite $CuHAsO_3$ will be formed (*distinction from* As_2O_5).

111. Place some granulated zinc into a test tube and cover it with dilute H_2SO_4, then add a solution of arsenic trioxide, obtained either according to 108 or 109, and gaseous arsenic trihydride AsH_3 (arsenetted hydrogen) will be evolved. Now cover the mouth of the test tube with a piece of filter paper moistened with a solution of mercuric chloride $HgCl_2$, and in a few moments the paper will be stained *yellow* to *orange red* (*characteristic test for arsenic*).

NOTE: This is the most convenient test for distinguishing between arsenic, antimony and tin. Antimony stains the paper *grey* to *black*, and tin produces no change whatever.

112. Marsh's Test.—Close the test tube as charged in the last experiment with a perforated stopper carrying a glass tube bent at right angles and drawn out to a point. After waiting a few minutes for the air to be expelled, ignite the jet of gas, and it will burn with a *bluish-white*

flame, while at the same time *white* fumes of As_2O_3 are evolved. In the inner portion of the flame the combustion is incomplete, and if the lid of a porcelain crucible or a porcelain dish be held in the flame, black spots of metallic arsenic, resulting from the decomposition of the AsH_3, will be deposited upon the surface. These spots dissolve readily in a solution of sodium hypochlorite NaClO, and by this means arsenic is characterized and distinguished from antimony.

113. Heat on charcoal with Na_2CO_3 some As_2O_3 or any compound of arsenious acid, and a characteristic *garlic* odor will be omitted.

ARSENIC COMPOUNDS.

Heat a small quantity of As_2O_3 in a test tube with concentrated HNO_3, and a solution of H_3AsO_4 will be obtained. Neutralize this solution with NaHO, and sodium arsenate Na_3AsO_4 will be formed. Employ this solution for the following tests:

114. To a portion of the solution add $AgNO_3$, and a *reddish-brown* precipitate of *silver arsenate* Ag_3AsO_4 will be produced. This precipitate is readily soluble in NH_4HO as well as in dilute HNO_3, and distinguishes arsenic acid from arsenious acid (109).

115. To another portion of the Na_3AsO_4 solution add a solution of $CuSO_4$, and a *light blue* precipitate of *copper hydrogen arsenate* $CuHAsO_4$ will be formed, which also distinguishes arsenic acid from arsenious acid (110).

116. To a third portion of the Na_3AsO_4 solution add NH_4Cl, NH_4HO and $MgSO_4$, and a white precipitate of *magnesium ammonium arsenate* $MgNH_4AsO_4$ will be formed.

NOTE: Arsenic compounds in acid solutions are reduced to arsenious compounds when treated with H_2S, and finally precipitated as arsenic trisulphide As_2S_3 mixed with free sulphur. The precipitation is much slower, than that of arsenious compounds, and may be accelerated by boiling the solution after treating with H_2S and then adding more. In experiments 111, 112 and 113, arsenic compounds behave just as arsenious compounds. None of these tests need be repeated.

ANTIMONY.

Antimony forms two series of compounds, the respective oxides of which are *antimonious* oxide Sb_2O_3, which plays the part of a base, and *antimonic* oxide Sb_2O_5, which is the anhydride of antimonic acid.

The tests given below for antimonious compounds apply equally well to antimonic compounds, and hence need not be repeated with substances of the latter series.

ANTIMONIOUS COMPOUNDS.

117. To a solution of an antimonious salt acidulated with HCl add H_2S, and an *orange red* precipitate of *antimonious sulphide* Sb_2S_3 will be formed, which is soluble in $(NH_4)_2S$ as well as in concentrated HCl.

118. To a neutral or slightly acid solution of an antimonious salt add a large quantity of water, and a *white* precipitate of a basic antimonious salt will be formed. In case of $SbCl_3$ this precipitate is *antimonious oxychloride* $SbClO$. This precipitate is readily soluble on addition of HCl, HNO_3 or H_2SO_4, and is distinguished from the corresponding compound of bismuth by being soluble in *tartaric acid* (see 106).

NOTE: Tartrates of antimony or other salts mixed with tartaric acid are not precipitated by water, but, if to these solutions HCl, HNO_3 or H_2SO_4 be added, the same white precipitate mentioned above will be produced.

119. Introduce into a test tube some granulated zinc and cover it with dilute H_2SO_4, then add a few drops of a solution of an antimonious salt, and antimony trihydride SbH_3 will be evolved. Now cover the mouth of the test tube with a piece of filter paper moistened with a solution of mercuric chloride $HgCl_2$, and in a few moments the paper will be stained *grey* to *black* (*characteristic test*). Compare note under 111.

120. Marsh's Test.—Close the test tube, as charged in the last experiment, with a perforated stopper carrying a glass tube bent at right angles and drawn out to a point. Wait a few minutes for the air to be expelled, then ignite the jet of gas, and it will burn with a *bluish green* tint, while at the same time heavy white fumes of antimonious oxide are evolved. Hold into the flame the lid of a porcelain crucible or a small porcelain dish, and black spots of metallic antimony, resulting from the decomposition of the SbH_3, will immediately be deposited upon the surface. These spots are not at all or very slowly removed by a solution of sodium hypochlorite (*characteristic test*). Compare arsenic 112.

121. Heat upon charcoal before the blowpipe with Na_2CO_3 any compound of antimony (excepting the sulphides), and *brittle* globules of metallic antimony will be formed, which are distinguished from bismuth, by evolving heavy white fumes when heated (*characteristic test*).

TIN.

Tin forms two series of compounds, the *stannous* compounds, among which may be mentioned stannous oxide SnO and stannous chloride $SnCl_2$, and the *stannic* compounds, among which may be mentioned stannic oxide SnO_2 and stannic chloride $SnCl_4$.

STANNOUS COMPOUNDS.

122. To a solution of a stannous salt add H_2S, and a *dark brown* precipitate of *stannous sulphide* SnS will be formed, which is soluble in $(NH_4)_2S$.

123. To a solution of a stannous salt add $HgCl_2$ in excess, and a *white* precipitate of *mercurous* chloride Hg_2Cl_2 will be formed, and the stannous salt will be converted into a stannic salt. (*Distinction from stannic salts.*) If the stannous salt is in excess the white Hg_2Cl_2 at first formed will be changed to grey metallic Hg.

124. Lay a platinum foil in a porcelain dish and place upon it a small fragment of metallic zinc, then add a solution of a stannous salt and a little HCl, and a spongy mass of metallic tin will be formed, which does not stain or adhere to the platinum foil. After the fragment of zinc has disappeared, add some concentrated HCl, and the metallic tin thus formed will readily dissolve (*characteristic test for tin* either as stannous or stannic compounds).

STANNIC COMPOUNDS.

A solution of a stannic salt may be conveniently prepared by heating a portion of the solution, employed in testing for stannous salts, with a little HNO_3.

125. To the solution thus obtained add H_2S, and a *yellow* precipitate of *stannic sulphide* SnS_2 will be formed, which is soluble in $(NH_4)_2S$.

Note: Stannic salts behave like stannous salts with zinc on platinum foil, and hence this test (124) is characteristic for tin in stannic compounds. Stannic salts are distinguished from stannous salts in that they do not reduce $HgCl_2$ to Hg_2Cl_2. (See 123.)

SCHEME IV.

TESTING FOR METALS OF GROUP IV.

(1) Dissolve the substance to be tested, if possible, in water, and to the solution add a few drops of dilute HNO_3.

No precipitate:	*A white precipitate:*
Absence of Sb in the form of a *tartrate*. Proceed with the same solution according to (2.)	Indication of Sb in the form of a *tartrate*. Ignore the precipitate and proceed according to (3.)

If the substance to be tested is insoluble in water, dissolve it in HNO_3 and proceed according to (2).

(2) To the solution add HCl.

<table>
<tr><td rowspan="3"><i>No precipitate:</i>
Absence of Pb, Ag, and Hg, as mercurous compounds. Proceed with the same solution according to (3.)</td><td colspan="3"><i>A white precipitate</i> ($PbCl_2$, AgCl or Hg_2Cl_2).
Add more water if necessary and boil:</td></tr>
<tr><td rowspan="2"><i>Precipitate dissolves:</i>
$PbCl_2$.
Confirm the presence of Pb by neutralizing the solution with NH_4HO, adding $C_2H_4O_2$ and finally $K_2Cr_2O_7$ (83).</td><td colspan="2"><i>Precipitate does not dissolve:</i>
Add NH_4HO in excess:</td></tr>
<tr><td><i>Precipitate dissolves completely:</i>
AgCl.
This test is characteristic for Ag (76).</td><td><i>Precipitate turns black:</i>
Hg_2Cl_2.
This test is characteristic for mercurous compounds (87).</td></tr>
</table>

(3) To the solution add H_2S, and the remaining metals of this group will be precipitated as follows :

As_2S_3—yellow.
Sb_2S_3—orange-red.
SnS_2—yellow.
SnS—brown.
HgS—black.
PbS—black.
Bi_2S_3—black.
CuS—black.
CdS—yellow.

Neutralize the free acid with NH_4HO and add $(NH_4)_2S$ in excess.

Precipitate dissolves.	*Precipitate does not dissolve.*
As_2S_3, Sb_2S_3, SnS_2 & SnS.	HgS, Pbs, Bi_2S_3, CuS, CdS.
Take some of the original substance or solution and test for :	Take some of the original substance or solution and test for :
As—According to (111) and distinguish As_2O_3 from As_2O_5 according to (109 and 114.) Sb—According to (119.) Sn—According to (124.)	Hg—According to (89 or 94.) Pb—According to (84 or 85.) Bi—According to (106.) Cu— " " (97 or 98.) Cd—Cadinnum is sufficiently confirmed by the yellow CdS insoluble in $(NH_4)_2S$.

SEPARATION OF GROUP IV.

Note: According to the reactions of the metals of this group given in the preceeding pages, they may be classed for convenience sake in three divisions:

DIVISION I.

Metals, which are precipitated by HCl, Pb, Ag and Hg (in mercurous compounds).

DIVISION II.

Metals, whose sulphides are insoluble in $(NH_4)_2S$, Hg, Pb, Bi, Cu and Cd.

DIVISION III.

Metals, whose sulphides are soluble in $(NH_4)_2S$, As, Sb and Sn.

1. To a solution of the metals of this group add HCl in excess and filter.

Precipitate (A) on filter contains $PbCl_2$, AgCl and Hg_2Cl_2.	Filtrate (B) contains Divisions II and III. (Preserve).

2. Wash precipitate (A) on filter with hot H_2O until nothing more dissolves.

<table>
<tr>
<td rowspan="2">*Solution* contains $PbCl_2$. Confirm presence of Pb by adding $K_2Cr_2O_7$ (84).</td>
<td colspan="2">*Residue* contains AgCl and Hg_2Cl_2. Treat residue on filter with NH_4HO.</td>
</tr>
<tr>
<td>*Solution* contains Ag. Confirm presence of Ag by acidifying the solution with HNO_3, which will reprecipitate AgCl.</td>
<td>*Residue* contains Hg. The *black* color of the residue is sufficient confirmation for the presence of mercurous compounds.</td>
</tr>
</table>

3. Dilute filtrate (B) with water and pass a current of H_2S gas through it for 10 or 15 minutes, then boil for a short time and finally pass a current of H_2S through it for 10 or 15 minutes longer. Filter and test filtrate with H_2S to see if all the metals have been precipitated ; if so, reject it.

Perforate the filter with a glass rod and wash the precipitate into a beaker, then add $(NH_4)_2S$ in excess. Stir the mixture well, allow the precipitate to subside and filter.

Precipitate (C) contains metals of Division II, as sulphides.	*Filtrate* (D) contains metals of Divisions III. (Preserve).

4. Wash precipitate (C) two or three times with water to remove any soluble chlorides, perforate the filter, wash the precipitate into a beaker with as little water as possible, then add concentrated HNO_3, boil and filter.

Residue on filter contains Hg as HgS. To confirm the presence of Hg, transfer the residue into a porcelain dish, add a few drops of HCl and HNO_3, heat and test solution with metallic copper (89).	*Filtrate* (E) contains Pb, Bi, Cu and Cd.

5. To the filtrate (E) add NH_4HO in excess and filter.

Precipitate contains Pb and Bi as hydroxides.

Pour some dilute H_2SO_4 on the filter, and when the liquid has run through, wash the residue once or twice with a little water.

Residue contains Pb as $PbSO_4$. Put some NH_4HO into a test tube, then add $HC_2H_3O_2$ in excess, heat the mixture and pour it on the residue, to dissole the $PbSO_4$. Then test for Pb with $K_2Cr_2O_7$ (84).

Solution contains Bi as $Bi_2(SO_4)_3$. Add NH_4HO in excess, filter the precipitated $Bi(HO)_3$, dissolve in the smallest possible quantity of dilute HCl, and add the solution to a large beaker full of water, which will confirm Bi (106).

Filtrate contains Cu and Cd.

The *blue* color of the solution is sufficient proof of the presence of copper.

Add to the solution potassium cyanide KCy until the blue color is entirely destroyed, then add $(NH_4)_2S$, and a yellow precipitate (CdS) will confirm the presence of cadimum.

6. Acidulate filtrate (D) with HCl, and the metals of Division III will be reprecipitated as sulphides. Filter and dry. When dry remove the precipitate from the filter, and mix it in a mortar with about twice its weight of dry KNO_3, and about twice its weight of dry Na_2CO_3. Heat some KNO_3 to fusion in a porcelain crucible, and without removing the lamp introduce the mixture just mentioned into the crucible little by lit-

tle, by means of a spatula or knife blade. When all has been added, pour the fused mass into a *perfectly dry* porcelain mortar. Pulverize finely, add H_2O filter and wash.

<table>
<tr><td colspan="2"><i>Residue</i> contains Sb as $Na_4Sb_2O_7$ and Sn as SnO_2. Pour on the filter a hot solution of tartaric acid and wash.</td><td rowspan="2"><i>Filtrate</i> contains As as Na_3AsO_4. Confirm presence of As by adding to the solution a mixture of $MgSO_4$ NH_4Cl and NH_4HO, which will precipitate white $MgNH_4AsO_4$(116)</td></tr>
<tr><td><i>Residue</i> contains Sn. Pour on the filter a hot solution of NaHO to dissolve the SnO_2, acidulate the solution with HCl and confirm the presence of Sn according to (124.)</td><td><i>Solution</i> contains Sb. Confirm the presence of Sb according to (119).</td></tr>
</table>

ACIDS.

INORGANIC ACIDS.

GROUP I.

Acids, whose combinations effervesce or yield a characteristic gas when treated with dilute HCl, *in the cold* (H_2CO_3, H_2S, H_2SO_3, $H_2S_2O_3$, HClO and HNO_2).

CARBONIC ACID H_2CO_3.

126. Introduce into a test tube any carbonate as $CaCO_3$ or Na_2CO_3 and add dilute HCl, and CO_2 will be evolved with effervescence. This gas is colorless and is distinguished from the other members of this group in being odorless.

127. Close the test tube in which CO_2 is evolved as above with a stopper provided with a delivery tube and conduct the gas into a small beaker containing some

clear lime water, and a white precipitate of $CaCO_3$ will be formed (*characteristic test*).

HYDROSULPHURIC ACID H_2S.

NOTE : The sulphides of the alkalies, the alkaline earths as well as those of iron, manganese and zinc are decomposed by dilute HCl with evolution of H_2S. All other sulphides yield H_2S with dilute HCl after fusion with Na_2CO_3 in a porcelain crucible owing to the formation of Na_2S.

128. Introduce into a test tube some FeS or $(NH_4)_2S$, then add dilute HCl, and H_2S will be evolved with effervescence, having the characteristic odor of rotten eggs.

129. Cover the mouth of the test tube, in which H_2S is evolved, with a piece of filter paper, moistened with a solution of $Pb(C_2H_3O_2)_2$, and the paper will be stained black, owing to the production of PbS [*characteristic test*].

SULPHUROUS ACID H_2SO_3.

130. To a strong solution of a sulphite as Na_2SO_3 add dilute HCl and SO_2 will be evolved with slight effervescence, having the pungent and suffocating odor of burning sulphur, while the solution remains perfectly clear (*characteristic test*).

131. To a solution of a sulphite add $BaCl_2$ and a white precipitate of barium sulphite $BaSO_3$ will be formed. Next add dilute HCl, and the precipitate will dissolve. To this solution add a few drops of HNO_3 and heat, and a white insoluble precipitate of barium sulphate $BaSO_4$ will be formed. This latter precipitate results from the oxidation of the H_2SO_3 to H_2SO_4 by the HNO_3. In the place of HNO_3 other oxidizing agents as Br or Cl may be employed.

THIOSULPHURIC ACID $H_2S_2O_3$.

132. To a solution of a thiosulphate (hyposulphite) as $Na_2S_2O_3$ add dilute HCl, and SO_2 will be evolved, while at the same time the liquid becomes turbid or white from the separation of free sulphur. The separation of free sulphur distinguishes $H_2S_2O_3$ from H_2SO_3.

HYPOCHLOROUS ACID HClO.

133. To a solution of a hypochloric as $Ca(ClO)_2$ add dilute HCl, and chlorine gas will be evolved, which may be recognized by its odor.

134. Introduce into a solution of a hypochlorite a piece of litmus paper, and it will soon become bleached white (*characteristic test*).

The bleaching is accelerated by the addition of some dilute HCl or other acid.

NITROUS ACID HNO_2.

135. To a solution of a nitrite as KNO_2 add dilute HCl, and nitrogen dioxide will be evolved. On coming in contact with the oxygen of the air it oxidises to nitrogen trioxide and tetroxide, which are revealed by their characteristic odor and reddish-brown fumes.

136. To a cold solution of a nitrite add *acetic acid* $HC_2H_3O_2$ and then a cold solution of ferrous sulphate $FeSO_4$, and a *dark brown* coloration will be produced, caused by the absorption of NO in the ferrous sulphate solution (*characteristic test*).

GROUP II.

ACIDS, WHICH YIELD PRECIPITATES WITH $BaCl_2$ INSOLUBLE IN HCL (H_2SO_4 AND H_2SiF_6). ONLY THE FORMER OF THESE ACIDS NEED BE STUDIED HERE.

SULPHURIC ACID H_2SO_4.

137. To a solution containing free H_2SO_4 or a soluble

sulphate add $BaCl_2$, and a white precipitate of barium sulphate $BaSO_4$ will be formed, which is *insoluble* in HCl or other acids (*characteristic test*).

138. To a solution containing free H_2SO_4 or a sulphate add $Pb(C_2H_3O_2)_2$, and a white precipitate of lead sulphate $PbSO_4$ will be produced.

GROUP III.

ACIDS, WHICH ARE PRECIPITATED BY A SOLUTION OF CALCIUM SULPHATE $CaSO_4$ ON ADDITION OF NH_4HO (H_3PO_4, H_2SiO_3, $H_2C_2O_4$ AND HF).

PHOSPHORIC ACID H_3PO_4.

139. To a *neutral* or *alkaline* solution of a phosphate as Na_2HPO_4 add $CaSO_4$, and white gelatinous precipitate of *calcium hydrogen phosphate* $CaHPO_4$ will be produced, which is soluble in acetic acid.

140. To a *neutral* or *alkaline* solution of a phosphate as Na_2HPO_4 add $BaCl_2$ and a white precipitate of $BaHPO_4$ will be formed, soluble in HCl.

141. To a solution of ammonium molybdate $(NH_4)_2MoO_4$ in nitric acid add a drop or two of a solution of a phosphate as Na_2HPO_4, and either at once, or on warming *gently*, a *yellow* precipitate will be formed (*characteristic test*).

NŏTE: In testing an unknown solution for phosphoric acid if the first drop or two added do not produce a precipitate in a short time on warming gently, then more of the solution may be added. It is necessary, however, to bear in mind, that the solution to be tested must be added drop by drop to the solution of ammonium molybdate, since the yellow precipitate is soluble in phosphoric acid, and is formed only when the ammonium molybdate is in large excess.

142. To a solution of a phosphate as Na_2HPO_4 add a mixture of $MgSO_4$, NH_4Cl and NH_4HO and a white precipitate of *ammonium magnesium phosphate* $MgNH_4PO_4$ will be formed (*characteristic test in the absence of arsenic acid.*)

SILICIC ACID H_2SiO_3.

143. To a neutral or alkaline solution of a silicate as Na_2SiO_3 add $CaSO_4$, and a white gelatinous precipitate of $CaSiO_3$ will be formed, which readily dissolves on addition of $HC_2H_3O_2$ in excess.

144. To a solution of a silicate as Na_2SiO_3 add HCl in excess and evaporate to dryness on a water bath, then moisten with HCl and add H_2O, and Silica SiO_2 will remain as an insoluble white powder (*characteristic test*).

OXALIC ACID $H_2C_2O_4$.

145. To a neutral or alkaline solution of an oxalate as $(NH_4)_2C_2O_4$ add $CaSO_4$, and a white pulverulent precipitate of calcium oxalate CaC_2O_4 will be formed, which remains undissolved on addition $HC_2H_3O_2$.

146. To a solution of oxalic acid or an oxalate, or to a mixture of the solid substances with a little water, add manganese dioxide MnO_2, and then a few drops of concentrated H_2SO_4, and CO_2 will be given off with effervescence (*characteristic test*).

HYDROFLUORIC ACID HF.

147. To a solution containing HF or a fluoride add $CaSO_4$ and then NH_4HO in excess, and a *transparent* gelatinous precipitate of calcium fluoride CaF_2 will be formed, which remains undissolved on adding $HC_2H_3O_2$ in excess.

148. Mix some finely powdered fluoride as CaF_2 in a platinum or injured porcelain crucible to a thin paste with concentrated H_2SO_4 and cover the crucible with a

watch glass, whose convex surface has been coated with paraffine or bees-wax, and partially laid bare by drawing lines through the coating with a sharpened lead pencil. In half an hour or more, especially if the crucible be gently warmed, on removing the paraffine, the lines will be found etched into the glass (*characteristic test.*)

GROUP IV.

ACIDS WHICH ARE PRECIPITATED BY $Ag.NO_3$ AFTER THEIR SOLUTIONS ARE ACIDIFIED WITH HNO_3, BUT ARE NOT PRECIPITATED BY $BaCl_2$ OR $CaSO_4$ (HCL, HBR, HI, HCY, H_3FeCy_6 AND H_4FeCy_6).

HYDROCHLORIC ACID HCl.

149. To some HCl add MnO_2 and heat, and chlorine gas Cl will be evolved, which may be recognized by its odor and by bleaching a piece of moistened litmus paper held in the gas (*characteristic test*).

150. To any chloride (excepting chloride of silver, lead, mercury and tin), add strong H_2SO_4 and MnO_2 and heat, and Cl will be evolved as in 149.

151. To a solution containing HCl or any chloride as NH_4Cl add $AgNO_3$, and a *white* precipitate of AgCl will be produced, which is insoluble in HNO_3, but *readily* soluble in NH_4HO. On exposure to light the precipitate turns *violet* and finally *black*.

152. To HCl or a solution of a chloride (not too dilute) add $Pb(C_2H_3O_2)_2$, and a *white* precipitate of Pb Cl_2 will be produced.

HYDROBROMIC ACID HBr.

153. To a bromide, as KBr, add strong H_2SO_4 and MnO_2 and heat, and *reddish-brown* fumes of Br will be evolved, having a suffocating odor resembling chlorine. Close the mouth of the test tube with a piece of filter

paper covered with moistened starch, and the starch will be colored *orange-red* (*characteristic test*).

154. To a solution of a bromide as KBr add Ag NO_3 and a *yellowish-white* precipitate of AgBr will be formed, which is insoluble in HNO_3, but soluble in NH_4HO, less readily, however, than the corresponding precipitate of AgCl. It blackens on exposure to light.

155. To a solution of a bromide as BKr add $Pb(C_2H_3O_2)_2$, and a white precipitate of Pb Br_2 will be produced.

HYDROIODIC ACID HI.

156. To an iodide as K I add strong $H_2 SO_4$ with or without MnO_2, and free iodine will be eliminated in the form of a *dark brown* powder with a characteristic odor resembling chlorine. On heating the test tube will be filled with beautiful violet-blue vapor of iodine. Close the mouth of the test tube with a piece of filter paper covered with moistened starch and heat so that the vapor will come in contact with the starch, and it will be colored *blue* (*characteristic test*).

157. To a solution of an iodide as K I add Ag NO_3, and a *yellowish-white* precipitate of Ag I will be formed, which is insoluble in HNO_3 and only very sparingly soluble in NH_4HO.

158. To a solution of an iodide as K I add $Pb(C_2H_3O_2)_2$, and a bright yellow precipitate of Pb I_2 will be formed.

HYDROCYANIC ACID HCy.

159. Place into a porcelain dish a small quantity of a solution containing HCy, or a soluble cyanide as KCy, add a few drops of yellow $(NH_4)_2S$ and digest on a water bath until the $(NH_4)_2S$ is destroyed, then acidulate with H Cl and add $Fe_2 Cl_6$, and a blood red solution of ferric sulphocyanide $Fe_2(CyS)_6$ will be formed (*characteristic test*).

160. To a solution containing H Cy or a cyanide as K Cy add $AgNO_3$ in excess, and a white precipitate of AgCy will be formed, which is insoluble in HNO_3, but soluble in KCy and in NH_4HO.

HYDROFERRICYANIC ACID $H_3 Fe Cy_6$.

161. To a solution of a ferricyanide as $K_3 FeCy_6$ add a solution of a ferrous salt as $Fe SO_4$, and a *dark blue* precipitate of ferrous ferricyanide $Fe_3(FeCy_6)_2$ (Prussian blue) will be formed (*characteristic test*).

162. To a solution of a ferricyanide as $K_3 FeCy_6$ add $Ag NO_3$, and an *orange-yellow* precipitate of silver ferricyanide $Ag_3 FeCy_6$ will be formed, insoluble in HNO_3, but soluble in NH_4HO.

HYDROFERROCYANIC ACID H_4FeCy_6.

163. To a solution of a ferrocyanide as K_4FeCy_6 add Fe_2Cl_6, and a *dark blue* precipitate of ferric ferrocyanide $Fe_4(FeCy_6)_3$ will be formed (*characteristic test*).

164. To a solution of a ferrocyanide as K_4FeCy_6 add $Ag NO_3$, and a *white* precipitate of silver ferrocyanide Ag_4FeCy_6 will be formed, insoluble in HNO_3 and in $NH_4 HO$.

GROUP V.

ACIDS, WHICH ARE NOT DETECTED IN EITHER OF THE FOREGOING GROUPS (HNO_3, $HClO_3$, HBO_2, H_2CrO_4 AND $HC_2H_3O_2$).

NITRIC ACID HNO_3.

165. To a solution of a nitrate as KNO_3 add an equal bulk of concentrated H_2SO_4 and cool the mixture ; then incline the test tube and pour carefully into it a cold solution of ferrous sulphate $FeSO_4$. Where the two layers of liquid meet a *dark brown* ring will appear, formed by the absorption of nitrogen dioxide NO in the ferrous sulphate solution [*characteristic test*].

166. Heat a small fragment of a nitrate as KNO_3 on charcoal before the blowpipe, and deflagration will ensue, *i. e.:* the surface of the charcoal will be violently attacked by the fused nitrate, the oxygen of the nitrate burning the carbon to CO_2.

CHLORIC ACID $HClO_3$.

167. Place a small fragment of a chlorate as $KClO_3$ into a test tube and pour upon it some concentrated H_2SO_4. The acid speedily assumes a *reddish-yellow* color and on shaking a yellow gas, chlorine tetroxide Cl_2O_4 is given off, having an odor resembling chlorine. On gently heating the mixture crackling sounds will be produced, caused by slight explosions of gaseous Cl_2O_4 [*characteristic test*].

NOTE : In making this experiment a *small* fragment of the chlorate only should be used and the mouth of the test tube should be held away from the experimenter, to avoid the possible danger of the hot acid being thrown upon him.

168. Heat a small fragment of a chlorate on charcoal before the blowpipe, and deflagration will take place.

BORIC ACID HBO_2.

169. Mix in a porcelain dish any borate as $Na_2B_4O_7$ with concentrated H_2SO_4, then add alcohol and after stirring the mixture ignite the alcohol and it will burn with a green flame, due to the volatilization and ignition of the boric acid (*characteristic test*).

CHROMIC ACID H_2CRO_4.

170. To a solution of a chromate as $K_2Cr_2O_7$ add $Pb(C_2H_3O_2)_2$ and a bright yellow precipitate of lead chro-

mate $PbCrO_4$ will be produced, insoluble in $HC_2H_3O_2$ (*characteristic test*).

171. To a solution of a chromate as $K_2Cr_2O_7$ add HCl and H_2S, and the reddish-yellow solution will turn green, owing to the reduction of the chromic acid to a chromic salt, while at the same time free sulphur separates, rendering the liquid turbid.

On account of this behavior with H_2S, chromates will, in the ordinary course of analysis, yield a precipitate of $Cr_2(HO)_6$ in the $(NH_4)_2S$ group of the metals.

ACETIC ACID $HC_2H_3O_2$.

172. To any acetate as $NaC_2H_3O_2$ add concentrated H_2SO_4 and about an equal bulk of alcohol, and on heating the mixture *acetic ether* $C_2H_5C_2H_3O_2$ will be produced which is recognized by its agreeable, fruity odor (*characteristic test*).

II. ORGANIC ACIDS.

$(H_2C_2O_4,\ HC_2H_3O_2$ and $H_2C_4H_4O_6)$

NOTE: The combinations of these acids burn when ignited in the air and yield residues, which are charred *i. e.*, blackened by separation of carbon. In regard to oxalic acid $H_2C_2O_4$ and acetic acid $HC_2H_3O_2$ this test may in some cases be overlooked; and hence these two acids have been considered in the proper groups of the inorganic acids.

OXALIC ACID $H_2C_2O_4$.

(See 145 and 146).

ACETIC ACID $HC_2H_3O_2$.

(See 172).

TARTARIC ACID $H_2C_4H_4O_6$.

173. Heat some tartaric acid or a tartrate as KHC_4

H_4O_6 on the lid of a porcelain crucible, and it will char, while at the same time the odor of *burnt sugar* will be evolved (*characteristic test*).

174. To a solution of ferric chloride Fe_2Cl_6 add tartaric acid or a tartrate in sufficient quantity and then NH_4HO in excess, and *no precipitate* of ferric hydroxide will be formed (*characteristic test*).

SCHEME V.

TESTING FOR ACIDS.

(1) Heat a small portion of the dry substance on a porcelain lid in the flame of a Bunsen burner.

It *chars or burns:* Presence of organic acids.

Test for tartaric acid according to 173 and 174.
“ “ oxalic “ “ “ 146.
“ “ acetic “ “ “ 172.

(2) To a portion of the solution, or of the dry substance add dilute HCl.

A GAS IS EVOLVED : GROUP I.

Test for H_2CO_3 according to 126 and 127.
“ “ H_2S “ “ 128 and 129.
“ “ H_2SO_3 “ “ 130 and 131.
“ “ $H_2S_2O_3$ “ “ 132.
“ “ $HClO$ “ “ 133 and 134.
“ “ HNO_2 “ “ 135 and 136.

(3) To a portion of the solution add a few drops of $BaCl_2$ and then HCl in excess.

A WHITE RESIDUE REMAINS : GROUP II. H_2SO_4.

(4) To another portion of the solution add HNO_3, $CaSO_4$ and then NH_4HO in excess.

A PRECIPITATE IS FORMED: GROUP III.

Add $HC_2H_3O_2$ in excess.

The precipitate dissolves: H_3PO_4 and H_2SiO_3.

Test for $H_3 PO_4$ according to 141 and 142.
“ “ $H_2 SiO_3$ “ “ 144.

The precipitate does not dissolve: $H_2C_2O_4$ and HF.
Test for $H_2C_2O_4$ according to 146.
“ “ HF “ “ 148.

(5) To another portion of the solution add HNO_3 and $AgNO_3$.

A PRECIPITATE IS FORMED: GROUP IV.

Add NH_4 HO in excess.

The precipitate dissolves: HCl, HBr, HCy, H_3FeCy_6.
Test for H Cl according to 150.
“ “ H Br “ “ 153.
“ “ H Cy “ “ 159.
“ “ H_3FeCy_6 “ “ 161.

The precipitate does not dissolve: H I and H_4FeCy_6.
Test for H I according to 156.
“ “ H_4FeCy_6 according to 163.

(6) There still remain to be tested the acids of Group V.

Heat a small quantity of the dry substance on charcoal before the blowpipe.

Deflagration takes place: H NO_3 and $HClO_3$.
Test for H NO_3 according to 165.
“ “ H ClO_3 “ “ 167.

No deflagration takes place: H BO_2, H_2CrO_4 and H $C_2 H_3 O_2$.
Test for H BO_2 according to 169.
“ “ H_2CrO_4 “ “ 170.
“ “ H $C_2H_3O_2$ “ “ 172.

(7) If no acid has been detected, the substance is an *oxide* or *hydroxide*.

ANALYSIS OF SUBSTANCES.

I. SIMPLE SUBSTANCES, I. E., SUBSTANCES CONTAINING ONE BASE AND ONE ACID—(A) SUBSTANCES SOLUBLE IN WATER—DETECTION OF THE BASE.

(1) Treat a solution of the substance in water according to Scheme IV, (1), (2) and (3).

(2) If no precipitate is formed (absence of metals of Group IV), add NH_4 Cl, then NH_4 HO until, after shaking, the solution smells of ammonia, and finally $(NH_4)_2S$. If a precipitate is formed proceed according to Scheme III.

(3) If no precipitate is formed (absence of metals of Group III), add $(NH_4)_2CO_3$ to the same solution. A white precipitate indicates Ba, Sr or Ca. Proceed according to Scheme II.

(4) If no precipitate is formed, add to the same solution Na_2HPO_4. A white precipitate proves the presence of Mg.

(5) If no precipitate is formed, the base is either K, Na or NH_4. Proceed with the original substance according to Scheme I.

DETECTION OF ACIDS.

After the base has been determined, a glance at Table III will show what acids are to be looked for.

(1) If the base belongs to Group I any one of the acids, which have been considered here may be present, since the metals of Group I, as shown by the table, form soluble compounds with all of them. Proceed for the detection of the acid according to Scheme V.

(2) If the base belongs to either Group II, Group III or Group IV, the acids of Group III can not be present, and hence test (4) of Scheme V may be omitted entirely.

So also the test for $H_2C_4H_4O_6$ may be omitted except in case of those compounds mentioned in the margin.

In like manner many other acids are shown to be absent.

TABLE III.

SHOWING THE SOLUBILITY OF SALTS IN WATER.

ACIDS.	GR. I.	GR. II.	GR. III.	GR. IV.	REMARKS.
$H_2C_4H_4O_6$	Sol.	Ins.	Ins.*	Ins.*	$Fe_2(C_4H_4O_6)_3$ Soluble.
$H_2C_2O_4$	Sol.	Ins.	Ins.	Ins.	$MnC_4H_4O_6$
$HC_2H_3O_2$	Sol.	Sol.	Sol.	Sol.	$CoC_4H_4O_6$
H_2CO_3	Sol.	Ins.	Ins.	Ins,	$SnC_4H_4O_6$
H_2S	Sol.	Sol.	Ins.	Ins.	$SbO)_2C_4H_4O_6$
H_2SO_3	Sol.	Ins.	Ins.	Ins.	
$H_2S_2O_3$	Sol.	Sol.	Sol.	Sol.	
HClO	Sol.	Sol.	Sol.	Sol.	
HNO_2	Sol.	Sol.	Sol.	Sol.	
H_2SO_4	Sol.	Ins.*	Sol.	Sol.*	Mg SO_4 Sol. Ca SO_4 Spar.Sol. $PbSO_4$ Ins.
H_3PO_4	Sol.	Ins.	Ins.	Ins	
H_2SiO_3	Sol.	Ins.	Ins.	Ins.	
HF	Sol.	Ins.	Ins.	Ins.*	AgF and HgF_2 soluble.
HCl	Sol.	Sol.	Sol.	Sol.*	AgCl and Hg_2Cl_2 Ins.
HBr	Sol.	Sol.	Sol.	Sol.*	AgBr,$Hg_2Br_2PbBr_2$Ins
HCy	Sol.	Sol.	Ins.	Ins.*	$HgCy_2$ soluble.
H_3FeCy_6	Sol.	Sol.	Ins.	Ins.	
HI	Sol.	Sol.	Sol.	Sol.	AgI, HgI_2 Hg_2I_2 PbI_2, Bi_2I_3, Ins.
H_4FeCy_6	Sol.	Sol.*	Ins.	Ins.	Ba_2FeCy_6 Insoluble.
HNO_3	Sol.	Sol.	Sol.	Sol.	Basic nitrate of Bi Ins.
HBO_2	Sol.	Ins.	Ins.	Ins.	
H_2CrO_4	Sol.	Sol.*	Ins.*	Ins.*	Ba CrO_4 Ins. Zn CrO_4 and $CuCrO_4$ Sol.
H_3AsO_3	Sol.	Ins.	Ins.	Ins.	
H_3AsO_4	Sol.	Ins.	Ins.	Ins.	
O	Sol.	Sol.*	Ins.	Ins.	MgO Insol.
HO	Sol.	Sol.*	Ins.	Ins.	$Mg(HO)_2$ Insoluble.

(B) SIMPLE SUBSTANCES INSOLUBLE IN WATER, BUT SOLUBLE OR DECOMPOSED BY ACIDS.

Under this head are included all those combinations, which are shown in Table III to be insoluble in water, with the exception of those treated of under (C.)

DETECTION OF THE BASE.

(1) Pulverize the substance finely in a mortar and treat a portion of it with concentrated HNO_3 applying heat if necessary. If it dissolves proceed with the solution according to the directions given under (A) for the detection of the bases of Group IV. (If insoluble in HNO_3 proceed according to (9).

(2) In case no metal of Group IV is present, the next step is to test for metals of Group III by adding to the same solution NH_4Cl, $NH_4 HO$ and $(NH_4)_2S$. By referring to Table III it will be seen that H_3PO_4, $H_2C_2O_4$, $H_2 SiO_3$, $H BO_2$ and HF form compounds with the metals of Group II, which are insoluble in water. These compounds all dissolve in HNO_3 (the fluorides with difficulty) and are reformed, when the acid is neutralized by NH_4HO and consequently the precipitate produced by $(NH_4)_2S$ may either be caused by a metal of Group III or it may be a *phosphate, oxalate, silicate, borate,* or *fluoride of calcium, barium, strontium* or *magnesium.*

If the precipitate is *black,* so as to leave no doubt that it is either FeS, CoS or NiS, it will be sufficient to test for these metals according to Scheme III, since only one base need here be looked for.

If however the precipitate is *light,* it will be necessary to insure the absence of the acids mentioned above, before any further tests can be made in a satisfactory manner. For this purpose proceed as follows:

(3) Heat another portion of the original powder to dull redness in a porcelain crucible. This will destroy

oxalic acid. Transfer the residue into a porcelain evaporating dish, add a large excess of concentrated HCl and evaporate to dryness on a water bath. By this operation HF and HBO_2 if present will be volatilized. Moisten the residue with H Cl, add water, and if all dissolves, proceed according to (7). If a white insoluble powder remains it is *silica*. Filter.

(4) To the filtrate add NH_4Cl, NH_4HO and $(NH_4)_2S$. If a precipitate is formed it is either $Al_2(HO)_6$, $Cr_2(HO)_6$ MnS or ZnS. Test according to Scheme III.

(5) If no precipitate is formed, add to the same solution $(NH_4)_2CO_3$. If a precipitate is formed proceed according to Scheme II.

(6) If no precipitate is formed by $(NH_4)_2CO_3$ add to the same solution Na_2HPO_4. A white precipitate proves the presence of Mg.

(7) In case no silica was detected above H_3PO_4 may still be present. Proceed as follows:

To the solution add Na_2CO_3 until the last drop or two cause a permanent precipitate, then add some $HC_2H_3O_2$ and finally $NaC_2H_3O_2$ in excess and boil. If a precipitate is formed, it is $Al_2(HO)_6$. Test according to (44).

(8) If no precipitate is formed, allow the liquid to cool, add Fe_2Cl_6 until it becomes colored red, then boil and filter. Reject the precipitate, which contains any H_3PO_4 present, and proceed with the filtrate as above (4), (5) and (6), bearing in mind, that Al has been shown to be absent (7).

(9) If the substance does not dissolve in HNO_3, heat another portion with concentrated HCl (If it does not dissolve proceed according to (10)). The most common substances, which are insoluble in HNO_3, but which will dissolve in HCl, are :

GROUP III.

MnO_2—black—evolves Cl with hot HCl.

Fe_2O_3—red to black—dissolves also in HNO_3.

Al_2O_3—white—dissolves also in HNO_3.

GROUP IV.

PbO_2—black—evolves Cl and is converted into white $PbCl_2$.

$2PbO, PbO_2$—red—evolves Cl and is converted into white $PbCl_2$. The PbO dissolves in HNO_3 and black PbO_2 remains.

$PbSO_4$—white—This compound is also treated of under (C), but it dissolves in a large excess of hot HCl, and the solution on cooling deposits white crystals of $PbCl_2$.

Sb_2O_3—white.

Sb_2O_5—white.

If the solution gives no indication of Pb through the separation of $PbCl_2$ add H_2S and proceed according to the directions given under (A).

(10) If the substance is insoluble in HNO_3(1) as well as in HCl(9) mix the contents of the two test tubes and heat. This mixture will yield nitro-hydrochloric acid. The only compound which will dissolve in nitro-hydrochloric acid after withstanding the action of HNO_3 and HCl separately, is mercuric sulphide HgS either *red* as vermilion or cinnabar, or *black* as obtained by precipitation with H_2S.

Proceed with solution according to the directions given under (A).

If the substance fails to dissolve in nitro-hydrochloric acid, pass on to (C).

DETECTION OF THE ACID.

(1) Proceed for the detection of the acid according to Scheme V.

NOTE 1. CO_2 and H_2S may already have been determined in testing for the base.

NOTE 2. If the substance is soluble in HNO_3, the presence of H_2SO_4 may be due to a sulphide, which is oxidized to a sulphate by the HNO_3. If the base belongs to Group IV, the sulphide will be insoluble in HCl and hence in order to determine whether the substance is a sulphide a small portion of it must be fused with about twice its weight of Na_2CO_3 in a porcelain crucible. By this means Na_2S is formed, which will evolve H_2S when treated with HCl (128 and 129).

NOTE 3 If the base be Pb, Ba or Sr it will have to be removed before test (4) can be applied, since these metals would be precipitated by $CaSO_4$ as sulphates. So also the metals of Group III and Group IV must be removed, since they are precipitated as hydroxides by NH_4HO and would thus interfere with the test. The removal of these bases is best accomplished by boiling the solution of the substance with an excess of Na_2CO_3, filtering and employing the filtrate for making the test, after decomposing the excess of Na_2CO_3 with HNO_3.

(C) SIMPLE SUBSTANCES INSOLUBLE IN ACIDS.

(1) The substances coming under this head are as follows:

GROUP II.

$BaSO_4$—white.

$SrSO_4$—white.

$CaSO_4$—white—sufficiently soluble in water to yield satisfactory tests for Ca and H_2SO_4.

GROUP III.

Cr_2O_3—green.

Fe_2O_3—red to black—when strongly ignited or in some form of minerals as specular iron ore.

Al_2O_3—white—when strongly ignited or in some form of minerals.

GROUP IV.

$PbSO_4$—white—soluble in a large excess of hot HCl.

$PbCl_2$—white—soluble in a large excess of hot HCl or water.

PbI_2—yellow.

AgCl—white—turns dark on exposure to light.

AgBr—yellowish—turns dark on exposure to light.

AgI—yellowish—turns dark on exposure to light.

SnO_2—white.

Also the following :

SiO_2—white.

S—yellow—burns to SO_2 when heated in the air.

C—black—burns up when heated on platinum foil in the air.

(2) Before substances of this class can be subjected to the systematic course of qualitative analysis, they must be rendered soluble. This is accomplished by fusion with Na_2CO_3 either in a porcelain or platinum crucible.

A preliminary examination, however, must precede the fusion, in order to determine if any reducible metals are present. For this purpose, heat a small portion of the substance on charcoal before the blowpipe with Na_2CO_3. If *metallic globules* are formed a *porcelain* crucible must be employed. If *no metallic* globules are formed a platinum crucible may be used.

(3) Mix a portion of the substance in a porcelain or platinum crucible, as the case may be, with about four times its weight of Na_2CO_3 and heat to fusion, if neces-

sary over the flame of a blowpipe. Place the crucible with the fused mass into a beaker with water and allow to digest until the mass has disintegrated. Then filter and wash. The *filter* will contain the base; the *filtrate* will contain the acid.

(4) Dissolve the residue on the filter in HNO_3, and proceed for the detection of the base according to the directions given under (A).

(5) Proceed with the filtrate for the detection of the acid according to Scheme V, (3), (4) and (5).

II. ANALYSIS OF COMPLEX SUBSTANCES.

(1) The analysis of complex substances is conducted in essentially the same manner as the analysis of simple substances.

When a precipitate is formed by a group reagent, however, it must be treated according to the directions given for the *separation* of that group, since more than one member of each group may be present. The reagent in each case must be added in excess to insure the complete precipitation of that group before filtering. The filtrate must be preserved for the next following group.

(2) If the substance is soluble in water no further directions need be given; but if it is insoluble, or only partly soluble in water, but dissolves in acids the separation of Group III must be slightly modified, on account of the possible presence of oxalates, phosphates, borates, &c., of the alkaline earths.

After filtering off the metals of Group IV or proving their absence, the solution or filtrate is evaporated to dryness, and heated to dull redness, to destroy $C_2H_2O_4$ and expel HBO_2. Residue is moistened with HCl, treated with water and filtered if any SiO_2 is present.

To the solution add NH_4HO and $(NH_4)_2S$ and filter. *Preserve filtrate.*

Proceed with the separation of the group according to the direction given until the manganese has been precipitated or proved to be absent. The solution may now contain not only Zn, but phosphates of the alkaline earths. Before proceeding further add Fe_2Cl_6 to the solution until it is colored slightly red, and boil. Filter off the precipitate, which will contain any H_3PO_4 and reject it.

Next test for Zn with $(NH_4)_2S$, and if any precipitate is formed, filter and add the filtrate to the one preserved above.

(2) Proceed with the united filtrates according to the directions given for the separation of Group II.

(4) The acids are detected according to Scheme V, following the directions given for simple substances.

ANALYSIS OF ALLOYS.

(1) In alloys only the metals of Group IV and Group III need to be looked for. Place a small portion of the alloy to be examined in a porcelain dish, add concentrated HNO_3 and evaporate to dryness on a water bath, moisten the residue with a few drops of HNO_3, add water and if a white powder remains undissolved, filter and proceed with the filtrate in the usual manner for the detection of the metals of Groups IV and III with the exception of Sn and Sb,

(2) The white insoluble powder may consist of SnO_2 and Sb_2O_5. Treat on the filter with a hot solution of tartaric acid, and confirm the presence of antimony in the solution according to (119).

Treat the residue if any with hot NaHO, accidulate with HCl and test for Sn according to (124).